REMARKS/ARGUMENTS

Reconsideration is respectfully requested of the Office Action of September 26, 2007 relating to the above-identified patent application.

The claims in the case are: Claims 9 to 20.

Claims 9, 17 and 18 have been amended to delete palladium. In addition, Claims 9, 10, 11, 18 and 19 have been amended to correct minor editorial matters. No new matter is presented by the foregoing amendments.

By way of background information, it is noted that two different processes for producing hydrogen cyanide from methane and ammonia are known to a person skilled in the art. For the convenience of the Examiner and to complete the record there is filed herewith a copy of an article from *Ullmann's Encyclopedia of Industrial Chemistry*, Fifth Edition, Vol. A8, pages 159-163. The first process is the reaction of methane and ammonia with oxygen to give hydrogen cyanide and water. This process is known to a skilled person in the art as the Andrussow process and is described in paragraph 1.2.1 (page161) of the *Ullmann's* article. The reaction of the Andrussow process is highly exothermic and occurs under oxidative conditions due to the use of oxygen as a reactant.

The second known process involves the reaction of methane and ammonia in the absence of oxygen to give hydrogen cyanide and molecular hydrogen. This process is known to the skilled person in this art as the BMA process and is described in paragraph 1.2.2 (page 162) of the enclosed *Ullmann*'s article. The reaction of the BMA process is endothermic and occurs under reductive conditions due to the formation of hydrogen.

Although both the Andrussow and the BMA process use a catalyst which comprises platinum as the major component, the two processes are substantially different in their reaction

conditions and therefore, a person skilled in this particular art would not expect that additional catalyst components would have the same suitability in both reactions. For example, aluminum nitride is a catalyst component suitable for the BMA process, but could not be used in a catalyst for the Andrussow process, because aluminum nitride would be oxidised to alumina at the oxidising reaction conditions of the Andrussow process. Therefore, based on his general knowledge about the fundamental differences between the Andrussow process and the BMA process as identified above (i.e. oxidation vs. reduction), a person skilled in this art would not expect that a catalyst component suitable for the Andrussow process would have the same suitability in the different BMA process.

The rejection of Claims 18-20 under 35 U.S.C. § 102(b) as anticipated, or alternatively under 35 U.S.C. § 103(a) in view of *Sperka, et al.*, (*Sperka*) U.S. 3,658,471, is traversed and reconsideration is respectfully requested.

Applicants respectfully submit that the amendment of Claim 18 deleting palladium overcomes the rejection under 35 U.S.C. § 102(b) in view of *Sperka*. This document does not disclose doping of platinum with copper, silver, gold or tungsten as called for by Claim 18.

All that *Sperka* suggests is to use combinations of platinum group metals, i.e. the doping of platinum with other platinum group metals. See col. 1, lines 58-65. More details of the platinum catalyst is given in col. 2, lines 1-7. The only substances that can be included with the platinum group metals in the catalyst are aluminum and/or magnesium; see col. 3, lines 12-16. Since none of the named doping elements of Claim 18 is a platinum group element, or aluminum and/or magnesium in combination with another platinum group metal, and since none of the named doping elements in Claim 18 is related to the platinum group members, or aluminium or

magnesium mentioned in the reference, applicants respectfully submit that *Sperka* does not create *prima facie* obviousness of the subject matter of Claims 18-20. No interchangeability has been shown between the *Sperka* catalysts and the catalysts of Claim 18.

The rejection of Claims 9, 10, 13 and 14 under 35 U.S.C. 102(b), or alternatively under 35 U.S.C. § 103(a) in view of US Published Application US 2002/31455 of *Hippel et al.*, (*Hippel*), is traversed and reconsideration is respectfully requested. *Hippel* '455 discloses in paragraph [0012] the use of a reactor containing separate heating channels and reaction channels running parallel to each other, which are separated from each other by walls consisting of a gas-impermeable material. The reaction channels contain a catalyst for the endothermic catalytic reaction, i.e. the reaction of methane and ammonia of the BMA process, and the heating channels contain a catalyst for the catalytic combustion of a fuel gas/air mixture, which is an exothermic reaction supplying the heat needed for the BMA process.

Paragraph [0014] explicitly states that the reactor is designed to prevent passage of the gases through the walls of the reaction channels into the heating channels. As a consequence, the reactant gases methane and ammonia fed to the reaction channels will not come into contact with the combustion catalyst that is located in the heating channels. Therefore, in the process disclosed by *Hippel* '455 methane and ammonia are <u>not</u> reacted in the presence of the combustion catalyst disclosed in paragraph [0025]. Instead, in the process of *Hippel* '455, the reaction of methane and ammonia is carried out in the presence of the reaction catalyst described in paragraph [0028]; namely platinum and aluminum nitride. As a consequence, *Hippel* '455 does not anticipate the subject matter of Claim 9 or any of the dependent Claims 10 to 17.

There is nothing in *Hippel* '455 that would suggest to a person skilled in the art to use the disclosed combustion catalyst as the reaction catalyst of the BMA process. Indeed, *Hippel* clearly teaches away from the present invention by specifying that the combustion catalyst and the reaction catalyst are separated by a gas impermeable wall. Since the combustion of a fuel gas/air mixture occurs by chemical reactions that are completely different from the reaction of methane and ammonia to form hydrogen cyanide, a person skilled in the art would have no reason to expect, that a catalyst suitable for catalysing a combustion reaction could also be suitable for catalysing the formation of hydrogen cyanide from methane and ammonia. Therefore, the subject matter of Claims 9, 10, 13 and 14 are not rendered *prima facie* obvious in view of the teachings of *Hippel* '455.

The rejection of Claim 10 under 35 U.S.C. § 103(a) as unpatentable in view of *Hippel* '455 taken with the *Benderly* published application, US 2005/0271572 A1, is traversed and reconsideration is respectfully requested. *Benderly* has a publication date of December 8, 2005.

The current application is a national stage of a PCT application that was published under Article 21(2) PCT in the English language as WO 2004/076351 A1. It is therefore entitled to a US filing date of February 18, 2004 for the application of 35 U.S.C. § 102(e), which is earlier than the filing date of *Benderly* of June 2, 2004. Therefore, *Benderly* does not qualify as prior art under 35 U.S.C. § 102 or § 103 for this application. To the contrary, this application is prior art to *Benderly* under 35 U.S.C. § 102(e).

Hippel '455 has already been discussed above and the remarks made there apply here as well.

Hippel '455 taken with *Benderly* does not anticipate or render obvious the claimed invention and therefore the rejection based on this combination of references should be withdrawn.

The rejection of Claims 9,10, 13 and 14 under 35 U.S.C. 102(e) or alternatively under 35 U.S.C. § 103(a) in view of *Benderly* is traversed and reconsideration is respectfully requested.

As already explained *Benderly* is not available as a reference against this application and therefore the rejection of the claims in view of *Benderly*, alone, should be withdrawn. *Benderly*'s filing date of June 3, 2004, does not pre-date applicants' international filing date under PCT of February 18, 2004.
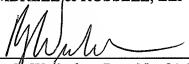
The indication of allowable subject matter is noted with appreciation.

Favorable action is requested at the Examiner's earliest convenience.

Respectfully submitted,

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Ullmann's   DK 66
Encyclopedia
of Industrial
Chemistry

Fifth, Completely Revised Edition

Volume A 8:
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Executive Editor: Wolfgang Gerhartz
Senior Editor: Y. Stephen Yamamoto
Editors: Lydia Kaudy, Rudolf Pfefferkorn,
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Cyano Compounds, Inorganic

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1. Hydrogen Cyanide

Hydrogen cyanide [74-90-8] (hydrocyanic acid, prussic acid, formonitrile), HCN, M_r 27.03, is a colorless liquid with the characteristic odor of bitter almonds. Hydrogen cyanide in aqueous solution was first prepared by SCHEELE in 1782 [18]. The acid occurs naturally in combination with some glucosides, such as amygdalin.

Hydrogen cyanide is currently produced by direct reaction of alkanes and ammonia, or indirectly as a byproduct in the manufacture of 2-propenenitrile [107-13-1] (by the ammoxidation of propene-acrylonitrile, Sohio process; → Acrylonitrile). Major end uses include the production of adiponitrile, methyl methacrylate,

cyanuric chloride, chelating agents, sodium cyanide, nitrilotriacetic acid, and methionine.

1.1. Properties

Physical properties [1], [19]–[22]:

Melting point	−13.24 °C
Boiling point	25.70 °C
Vapor pressure (0 °C)	35 kPa (0.35 bar)
(20 °C)	83 kPa (0.83 bar)
(50 °C)	250 kPa (2.5 bar)
Enthalpy of formation, ΔH	3910 kJ/kg
Critical temperature	183.5 °C
Critical density	0.20 g/cm³
Critical pressure	5 MPa (50 bar)
Density (20 °C)	0.687 g/cm³
Specific heat, liquid (20 °C)	2630 J kg⁻¹ K⁻¹

Specific heat, gas (25 °C)	1630 J kg^{-1} K^{-1}
Heat of fusion	310 kJ/kg
Heat of vaporization	935 kJ/kg
Heat of polymerization	1580 kJ/kg
Explosive range in air	5.5–46.5 vol %
Flash point	−17.8 °C
Ignition temperature	535 °C
Dynamic viscosity, η (20 °C)	0.192 mPa · s
Surface tension (20 °C)	18.33 mN/m
Dielectric constant (0 °C)	158.1
(20 °C)	114.9
Dissociation constant	
aqueous solution, pK (20 °C)	9.36

As a result of its high dielectric constant, HCN has acquired some importance in preparative chemistry as a nonaqueous, ionizing solvent [23].

Chemical Properties. Some comprehensive reviews on hydrogen cyanide and cyanogen compounds have been published [1]–[3]. The acid is found only in the nitrile form. Although isomeric isonitrile, HNC, has been detected in interstellar space, all efforts to isolate this compound have failed. As the nitrile of formic acid, HCN undergoes many typical nitrile reactions. For example, hydrogen cyanide can be hydrolyzed to formic acid by aqueous sulfuric acid or hydrogenated to methylamine. Hydrogen cyanide adds on to carbon–carbon double bonds, and it forms cyanohydrins with carbonyl groups of aldehydes or ketones. The most important uses of this type are in the manufacture of acetone cyanohydrin (an intermediate in the production of methyl methacrylate) and in the production of adiponitrile from butadiene and hydrogen cyanide. Another example is the multistep synthesis of amino acids via hydantoins. Hydrogen cyanide can be oxidized by air over silver or gold catalysts at 300–650 °C to yield cyanic acid (HOCN) and cyanogen (CN)$_2$ in an approximate 2:1 ratio.

The reaction of hydrogen cyanide with chlorine gives cyanogen chloride (see p. 181). For industrial purposes, the latter compound is usually directly trimerized to cyanuric chloride, the starting material for the chemistry of s-triazines.

In the presence of oxygen or air, hydrogen cyanide burns with a very hot flame. For the reaction

$$2\,HCN + 1.5\,O_2 \longrightarrow N_2 + 2\,CO + H_2O$$

the heat of formation is calculated to be −723.8 kJ/mol and the adiabatic flame temperature is 2780 °C. Pure liquid or gaseous HCN is

inert to most metals and alloys such as aluminum, copper, silver, zinc, and brass.

At higher temperatures (> 600 °C), the acid reacts with metals that can form carbides and nitrides (titanium, zirconium, molybdenum, and tungsten). Therefore, containers of unalloyed steel are used for storage and transportation of liquid anhydrous hydrogen cyanide.

Pure liquid hydrogen cyanide has a tendency to polymerize to brown-black, amorphous polymers, commonly called azulmic acid [26746-21-4]. The reaction is accelerated by basic conditions, higher temperature, UV light, and the presence of radicals. Since the decomposition is exothermic, the polymerization reaction is autocatalytic and can proceed with explosive violence to form the HCN dimer, iminoacetonitrile [1726-32-5], and the HCN tetramer, diaminomaleonitrile [1187-42-4], as intermediates [24], [25]. Both compounds are presumed to be important in the evolution of life, and cyano compounds may play a role in prebiotic syntheses [26], [27]. In the liquid phase, hydrogen cyanide is stabilized by the presence of small amounts of acids (0.1 wt % H$_3$PO$_4$, 1–5% HCOOH or CH$_3$COOH) or of 0.2 wt % SO$_2$ in the gaseous phase.

The HCN–H$_2$O System. At 25 °C, hydrogen cyanide is miscible with water in all ratios. The solution is a weak acid, with a dissociation constant of the same order of magnitude as amino acids. The relation between total cyanide concentration ($c_{HCN} + c_{CN^-}$) and dissociated cyanide (c_{CN^-}) in a dilute aqueous solution, as a function of pH, is illustrated in Figure 1.

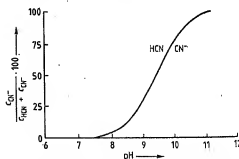Figure 2 shows the liquid–vapor equilibrium diagram at atmospheric pressure. Because of the

Figure 1. Dissociation of HCN in aqueous solution as a function of pH, based on total cyanide concentration $c_{HCN} + c_{CN^-}$
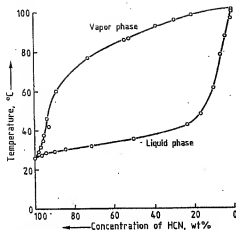
Figure 2. Liquid–vapor diagram of the system H₂O–HCN at atmospheric pressure

high HCN partial vapor pressure it is difficult to separate the acid from a gas mixture by absorption in water, which is an important consideration for industrial practice [28].

The stability of hydrogen cyanide solutions depends on the degree of dilution: at concentrations below 0.1 mol/L HCN, the acid is stable; addition of traces of acid prevents decomposition. Like pure HCN, the exothermic polymerization of an aqueous solution is accelerated by the presence of alkali. In addition to azulmic derivatives, small amounts of amino acids and purine bases are formed. This fact is of some importance to biological chemistry. The $C \equiv N$ triple bond is hydrolyzed by strong alkali or acid to give formic acid and ammonia. Higher temperatures or hydrothermal conditions favor these reactions.

1.2. Production [1], [29], [30]

Hydrogen cyanide can be produced when sufficient energy is supplied to any system containing the elements hydrogen, nitrogen, and carbon. Generally, only processes starting from hydrocarbons and ammonia are of economic importance today; however, the production of hydrogencyanide from formamide [31] is carried out in one plant at Ludwigshafen in the Federal Republic of Germany. Recent patents indicate interest in alternative raw materials such as methanol, carbon, or carbon monoxide [32]–

[41]; however, these routes have little chance of competing with present technology. The reaction of hydrocarbons and ammonia

$$C_n H_{2n+2} + x NH_3 \longrightarrow x HCN + 2 \cdot (2x + 1) H_2$$
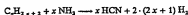
is highly endothermic and needs a continuous heat supply. The means of providing this energy requirement are manifold and characteristic of the different processes [42]. Only three of them are currently used to make hydrogen cyanide: the Andrussow ammoxidation process, which involves the reaction of ammonia, methane, and air over a catalyst gauze; and the two ammonia dehydration routes, the methane–ammonia (BMA) and the Shawinigan processes, developed by Degussa and Gulf Oil Company, respectively. The latter are performed in externally heated ceramic tubes or in an electrically heated fluidized coke bed. Twenty percent of the hydrogen cyanide in the United States and nearly 45% in Western Europe is obtained as a byproduct in the manufacture of acrylonitrile (2-propenenitrile) by the oxidation of propene in the presence of ammonia (Sohio technology).

1.2.1. Andrussow Process

The Andrussow process was developed around 1930 by L. ANDRUSSOW of I.G. Farben [43]–[45] and is currently the most important method for direct synthesis of hydrogen cyanide. The average capacity of single commercial installations is 5–30 × 10³ t/a; plants are operated by Du Pont, Rohm and Haas, and Monsanto in the United States; ICI, Butachemie, and Monsanto in Western Europe; and Kyowa Gas in Japan.

Figure 3 is a flow diagram of the Andrussow process. Natural gas, essentially methane purified from sulfur, is mixed with ammonia which flows from an evaporator. Compressed air is added in a volume ratio, corresponding closely to the theoretical reaction [46]:

$$CH_4 + NH_3 + 1.5 O_2 \longrightarrow HCN + 3 H_2O \quad \Delta H = -474 \, kJ/mol$$

The mixture is passed over a platinum–rhodium or platinum–iridium gauze [47] catalyst; temperature and upper flammable limit should be monitored carefully [48], [49]. The reaction takes place at > 1000 °C, at around atmospheric pressure, and with a gas velocity through the catalyst zone of about 3 m/s. To avoid decomposition of HCN, the effluent gas from the reactor is quickly
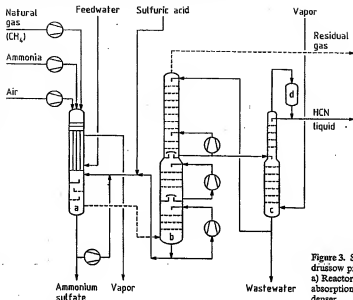
Figure 3. Simplified diagram of the Andrussow process
a) Reactor and ammonia scrubber; b) HCN absorption tower; c) HCN rectifier; d) Condenser

cooled in a waste-heat boiler, which produces the steam used in the process.

After the waste-heat boiler, the gas is washed with dilute sulfuric acid to remove unreacted ammonia: this is necessary to prevent polymerization of HCN. Because disposal of the resulting ammonium sulfate solution is expensive, other systems have been patented [50]–[52]. Alternatively, the off-gas from the ammonia scrubber is passed through a monoammonium phosphate solution [53], [54], where the ammonia reacts to form diammonium phosphate. To effect thermal reversal of the phosphate equilibrium, the absorption solution is boiled in a stripper by injection of steam. The ammonia released is condensed and recycled to the reactor, while the regenerated monoammonium phosphate solution is pumped back to the absorber.

After the ammonia scrubber, the gas is passed through a countercurrent column where the hydrogen cyanide is absorbed in cold water and the resultant solution is stabilized by adding acid (ca. 0.1 %). The hydrogen cyanide is stripped from the aqueous solution in a rectifier and condensed. The end product is highly pure and has a water content of less than 0.5 %. The aqueous absorber solution, containing traces of HCN, is cooled and fed back to the absorption tower. The residual gases, H_2, CO, and N_2, can be used for heating or methanated in a separate

unit and recycled as feedstock for HCN manufacture [55].

The advantages of the Andrussow process include (1) long catalyst life, up to 10 000 h; (2) well-tested technology, with a simple and safe reaction system; and (3) high-purity HCN. One disadvantage is the fact that the process is uniquely dependent on pure methane as a raw material as a result of severe carburization of the platinum catalyst; for example, a small percentage of higher hydrocarbon impurities rapidly causes trouble in the catalyst system and reduces conversion rates. Other important poisons for platinum are sulfur and phosphorus compounds. A further problem is the relatively low yield based on carbon (60–70 %) and ammonia (70 %), as well as the low hydrogen cyanide concentration in the product gas, so that recovery equipment must be built to handle large volumes of gas.

The compositions of reaction and residual gases in the Andrussow and BMA processes are compared in Table 1.

1.2.2. Methane–Ammonia (BMA) Process

The basis of the Degussa BMA process is the formation of hydrogen cyanide in the absence of oxygen [56]–[60]. The reaction
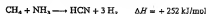
$$CH_4 + NH_3 \longrightarrow HCN + 3 H_2 \qquad \Delta H = + 252 \text{ kJ/mol}$$

Table 1. Composition of off-gases and residual gases (volume fractions, %) on the basis of pure methane and ammonia in the BMA and Andrussow processes

Compound	BMA		Andrussow*	
	After reaction	Residual	After reaction	Residual
HCN	22.9	<10⁻²	8.0	<10⁻²
NH₃	2.5	<10⁻²	2.5	> 0
H₂	71.8	96.2	22.0	24.6
N₂	1.1	1.5	46.5	51.9
CH₄	1.7	2.3	0.5	0.6
CO			5.0	5.6
H₂O			15.0	16.8
CO₂			0.5	0.6

Table 1. Composition of off-gases and residual gases (volume fractions, %) on the basis of pure methane and ammonia in the BMA and Andrussow processes

Compound	BMA		Andrussow*	
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HCN	22.9	$<10^{-2}$	8.0	$<10^{-2}$
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H₂	71.8	96.2	22.0	24.6
N₂	1.1	1.5	46.5	51.9
CH₄	1.7	2.3	0.5	0.6
CO			5.0	5.6
H₂O			15.0	16.8
CO₂			0.5	0.6

* Calculated because no consumption figures are available so far.

is endothermic, requires temperatures above 1200 °C, and is performed in externally heated, alumina tube bundles, which are coated with a thin layer of a special platinum catalyst [61], [62]. Several of these bundles are fixed in a reaction furnace unit. A mixture of ammonia and methane (natural or refined gas with a content of 50–100 vol % methane) is passed through the tubes and quickly heated to 1300 °C at normal pressure. To avoid the formation of any disturbing deposits of carbon black, the NH₃:CH₄ ratio is kept between 1.01 and 1.08. After leaving the reaction tubes, the product gas is cooled to 300 °C by passage through a water-cooled chamber made of aluminum. A kinetic study has shown that a particular temperature profile is essential for the reaction [63].

The subsequent reaction steps, ammonia absorption and hydrogen cyanide isolation, are similar to those of the Andrussow process. A distinct advantage is the higher HCN content (Table 1) of the off-gas, so that the number of steps, and the size and cost of recovery equipment, are greatly reduced. The tail gas consists mainly of pure hydrogen. If this is not needed for other syntheses, it can be used as fuel gas for heating the furnace. About 80–85 % of the ammonia and 90 % of the methane are converted to hydrogen cyanide. The specific energy consumption of ca. 4 × 10⁶ kJ/100 kg HCN reported thus far has been considerably decreased by recent developments [64], [65]. A large part of the heating energy is recovered and used in the air preheater or steam generator.

If the methane supply is limited or costly, the process can be carried out directly with liquefied hydrocarbons or ethanol, or in a three-step reaction starting from methanol [66]–[68]. Both Degussa and Lonza utilize the BMA route to produce hydrogen cyanide.

1.2.3. Shawinigan Process

In the Shawinigan process, hydrocarbon gases are reacted with ammonia in an electrically heated, fluidized bed of coke. The process, sometimes called the Fluohmic process, was developed in 1960 by Shawinigan Chemicals [69]–[72], now a division of Gulf Oil Canada.

In a circular reaction cavity constructed from alumina and silicon carbide, the mixture of ammonia and hydrocarbon (N:C-ratio slightly > 1) passes through a fluidized bed of coke, heated by electrodes immersed in the bed. The chemical reaction is similar to the methane–ammonia process, but no catalyst is required and temperatures are kept above 1500 °C. Other carbon compounds, such as naphtha or lighter hydrocarbons, can also be converted. Propane is usually the main feedstock. The reaction can be described as

$$3\,NH_3 + C_3H_8 \longrightarrow 3\,HCN + 7\,H_2 \qquad \Delta H = + 634\,kJ/mol$$
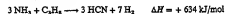
Unreacted feed gas is almost completely decomposed to the elements. This reduces the quantity of ammonia to be removed from the product gas and leads to the formation of coke particles. The control of bed coke size is an important operating parameter.

The reactor effluent contains up to 25 vol % HCN, 72 vol % H₂, 3 vol % N₂, and only 0.005 vol % NH₃. Coke is removed in a water-cooled, cyclone-entrained bed. The gas is further cooled and enters the absorption equipment where HCN is removed. The residual gas, nearly pure hydrogen, can be used for other chemical processes. Some of the hydrogen is recycled to the reaction unit to inhibit the formation of soot.

Coke from the cyclone is screened, and three fractions are separated, stored, and then batched back to the reactor system in the desired proportions to control the particle size distribution. By regulating the rate of coke recycling, the level of the fluidized bed and the reaction temperature can be controlled.

In practice, at least 85 % of the ammonia and up to 94 % of the hydrocarbon are converted to hydrogen cyanide. Because of the high electric power consumption (6.5 kW h per kilogram of HCN) the Shawinigan process would probably